

Heavy-Electron Behavior and Structural Change in $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$

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Sr_2RuO_4 is an unconventional superconductor with a tetragonal structure, whereas Ca_2RuO_4 is a Mott insulator with orthorhombic symmetry. The substituted $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ has yielded a rich phase diagram that is just beginning to be explored in detail. Experimental investigation of the resistivity ρ , susceptibility χ , specific heat C_p , Hall coefficient R_H , and X-ray diffraction of $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ reveals a structural phase transition near $T_0 = 190$ K and heavy-Fermion (HF) behavior below a coherence temperature $T^* \sim 10$ K, resembling that of the f -electron HF compound UPt_3 . The observation of T^2 -dependence of ρ below ~ 0.5 K suggests a Fermi-liquid ground state. Based upon our data and theoretical calculations, we argue that the structural change at T_0 may be responsible for the formation of the HF state.

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The discovery of unconventional superconductivity in Sr_2RuO_4 has stimulated great interest in the electronic properties of ruthenates. Despite its high electrical conductivity, a rather large ratio of the Coulomb repulsion (U) to the bandwidth (W) indicates that Sr_2RuO_4 is close to a Mott transition.[1] Both strong electron-electron correlations and Fermi-liquid (FL) ground state appear to play a crucial role in its physical properties. In particular, intriguing connections have been revealed between these correlations and unconventional superconductivity. The partial substitution of the smaller Ca^{2+} for Sr^{2+} changes both U and W , leading to rich and unusual phenomena in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$. [2] With increasing Ca content (decreasing x), superconductivity is rapidly destroyed and the in-plane resistivity ρ_{ab} increases, turning into insulating behavior ($d\rho_{ab}/dT < 0$) as $x < 0.2$. [2] This is consistent with the expected increase in the density of states (DOS) associated with the band narrowing due to the Ca substitution. [3, 4] However, the magnetic properties are not in complete accord with this picture. It was found that the low-temperature paramagnetic susceptibility increases with Ca concentration, peaking at $x = x_c = 0.5$. [5] Near this critical concentration, the effective magnetic moment tends to saturate with $S = 1/2$, [2] unexpected from band-structure calculations. [3] Neutron diffraction results suggest that the crystallographic distortion in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ may lead to a variation in the shape and the effective filling of the triply degenerated Ru t_{2g} bands through a Jahn-Teller (JT) type orbital rearrangement. [6] Of particular interest is the intermediate regime with $0.2 \leq x \leq 0.5$, where an electronic state containing both localized and itinerant electrons is proposed. [3]

In this Letter, we report the electronic, magnetic and thermodynamic properties of $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ ($x \sim 0.3$) single crystals. Investigation of the specific heat C_p and c -axis resistivity ρ_c indicates a continuous phase transition at $T_0 \sim 190$ K. Consistent with previous results, [2, 6] a structural transition from tetragonal ($T > T_0$) to orthorhombic ($T < T_0$) symmetry is observed. This leads to the deviation of the magnetic susceptibility χ from simple Curie behavior above T_0 to Curie-Weiss-like character below T_0 . Remarkably, the Hall coefficient R_H , measured by applying H perpendicular to ab -plane ($H \parallel c$), behaves similarly to $\chi_c(H \parallel c)$: $R_H(T)$ scales with $\chi_c(T)$ above $T^* \sim 10$ K, a characteristic temperature corresponding to a maximum χ_c and R_H . This behavior has been attributed to skew scattering due to magnetic moment effects in heavy-fermion (HF) systems such as UPt_3 . [7] Surprisingly, the resistivity $\rho_{ab,c}$ and specific heat C_p also reveal features remarkably similar to those of UPt_3 below T^* . A large Sommerfeld coefficient $\gamma = 266$ mJ/mol-K² also provides evidence for HF behavior in $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$, unexpected in a $4d$ -electron material exhibiting HF behavior. In contrast to previous conclusions based upon resistivity measurements above 0.3 K [5], we find that the resistivities $\rho_{ab,c}$ follow T^2 -dependence below ~ 0.5 K, showing a recovery of a Fermi-liquid ground state in the high Ca concentration regime. Again, this is similar to what is observed in UPt_3 . We discuss this heavy-electron behavior in terms of recently developed theoretical models.

Single crystalline $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ was grown using an NEC SC-M15HD image furnace. For feed-rod preparation, a mixture of CaCO_3 , SrCO_3 and RuO_2 , with molar ratio of 1.70:0.30:1.15, was pre-reacted in air at 1100 °C for 12 h. After regrinding, the powder was pressed into rods and heated in air at 1100 °C for another 12 h. Single crystals were grown using a feed rate of 30 mm/h and a

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T (K)	200 K	160 K	140 K	120 K	100 K
a (Å)	5.320(2)	5.310(2)	5.308(3)	5.307(1)	5.305(2)
b (Å)	5.320(2)	5.316(1)	5.319(1)	5.321(1)	5.322(1)
c (Å)	12.551(7)	12.546(3)	12.542(3)	12.541(4)	12.537(2)
vol. (Å ³)	355.2(2)	354.1(1)	354.3(2)	354.1(2)	354.0(3)

TABLE I: Lattice parameters and lattice volume in $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ at $T = 200, 160, 140, 120$ and 100 K.

growth rate of 15 mm/h in an atmosphere of 10% oxygen and 90% argon. Shiny black crystals are produced with actual Ca:Sr $\sim 1.7:0.3$ as determined by energy dispersive X-ray analysis. The crystal structure was refined using an Enraf-Nonius four-circle autodiffractometer with Mo $K\alpha$ radiation and a nitrogen-gas-stream cryocooler. Table I presents the lattice parameters at various temperatures between 100 and 200 K. Note that $a < b$ at $T < 200$ K, indicating that the system undergoes a structural change from tetragonal at high temperatures to orthorhombic symmetry at low temperatures, in good agreement with that obtained by neutron diffraction.[6]

As given in Table I, there is no drastic change in cell volume between 160 and 200 K. Below 160 K, the refinement data show negative thermal expansion along the b -axis while both a and c continuously decrease with decreasing T . These results suggest that the structural phase transition is continuous. This is confirmed by specific heat data. Fig. 1 shows the temperature dependence of the specific heat C_p of a $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ single crystal between 0.38 and 300 K. Note a kink occurs at a characteristic temperature $T_0 \sim 190$ K, corresponding to the structural phase transition. No hysteresis was observed in specific heat, which is consistent with a continuous phase transition.

For a non-magnetic metallic solid, the low-temperature specific heat C_p is usually analyzed by considering contributions from electrons ($C_p^e = \gamma T$) and lattice ($C_p^l = \beta T^3$), i.e., $C_p = \gamma T + \beta T^3$. Here, γ and β are T -independent constants. Thus, a plot of C_p/T vs. T^2 should be linear. For $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$, the temperature dependence of C_p/T between 0.38 and 20 K is shown in the inset of Fig. 1. The nonmonotonic T^2 -dependence of C_p/T with a dip at $T^* \sim 10$ K indicates a departure from normal metallic behavior in $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$. We recall that a similar temperature dependence of C_p/T has been seen in HF materials,[8] which can be expressed as [9]

$$C_p = \gamma T + \beta T^3 + \delta T^3 \ln(T/T_i), \quad (1)$$

where δ and T_i are constants. The last term describes the contribution from interactions between quasiparticles due to spin fluctuations, where T_i is a cut-off temperature with regard to the spin fluctuations.[8, 9] Using Eq. 1 to fit our specific heat data between 0.38 and 13 K yields that $\gamma = 266$ mJ/mol-K², $\delta = 1.86$ mJ/mol-K⁴ and $\beta\delta\ln T_i = -5.48$ mJ/mol-K⁴. As illustrated in the

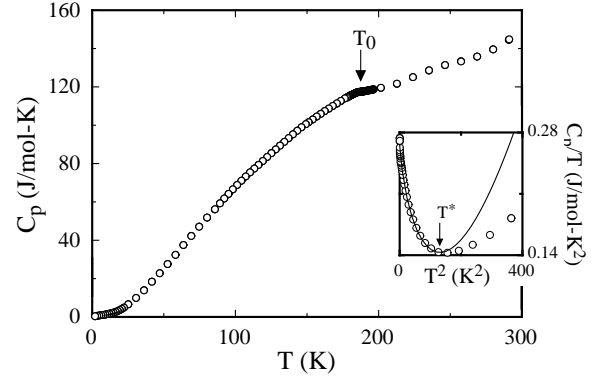


FIG. 1: Temperature dependence of the specific heat of a $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ single crystal between 0.38 and 300 K. Note a kink occurs at $T_0 \sim 190$ K. The inset is the specific heat data between 0.38 and 20 K plotted as C_p/T vs. T^2 . Note that C_p/T reaches a minimum at $T^* \sim 10$ K. The solid curve is the fit of experimental data between 0.38 and 13 K to Eq. 1 (see the text).

inset of Fig. 1 by the solid line, the above formula fits the experimental data (0.38 - 13 K) quite well.

The γ value extracted from the above fitting procedure is large compared with the parent compound Sr_2RuO_4 ($\gamma = 37.5$ mJ/mol-K² [10]) and is comparable to HF materials such as UPt_3 ($\gamma = 422$ mJ/mol-K² [11]). Heavy-electron behavior was first recognized in f -electron systems. Recently, similar behavior has also been seen in the 3d transition metal oxide LiV_2O_4 . [12] In general, HF behavior is not anticipated in systems containing 4d/5d electrons because of the extended nature of these orbitals.

In a Fermi-liquid system, information about the effective mass of the quasiparticles can be extracted from the low-temperature electrical resistivity when expressed as $\rho = \rho_0 + AT^2$ as $T \rightarrow 0$ K. Here, the residual resistivity ρ_0 and coefficient A are constants. According to Kadowaki and Woods (KW), the ratio A/γ^2 is expected to approach the universal value $A/\gamma^2 = 1.0 \times 10^{-5} \mu\Omega \text{ cm}/(\text{mJ/mol-K})^2$, if the electronic conduction and specific heat are governed by the same quasiparticles.[13] Shown in Fig. 2 are the temperature dependences of the ab -plane and c -axis resistivities of $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ between 0.05 and 300 K, measured using a standard four-probe technique. Note that ρ_{ab} increases with temperature ($d\rho_{ab}/dT > 0$), reflecting the itinerant nature of electrons. The c -axis resistivity ρ_c , however, undergoes a crossover from metallic behavior ($d\rho_c/dT > 0$) at $T < T_0$ to non-metallic character ($d\rho_c/dT < 0$) at $T > T_0$. Although ρ_{ab} and ρ_c of $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ superficially resemble those of undoped Sr_2RuO_4 , it is clear that the metallic-nonmetallic transition in ρ_c of $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ is due to the structural change, which shortens the lattice parameter c and subsequently enhances the interlayer coupling below T_0 . Interestingly, ρ_{ab} remains metallic without any noticeable anomaly, although lattice parameters a and b are also spontaneously changed (see Tab.

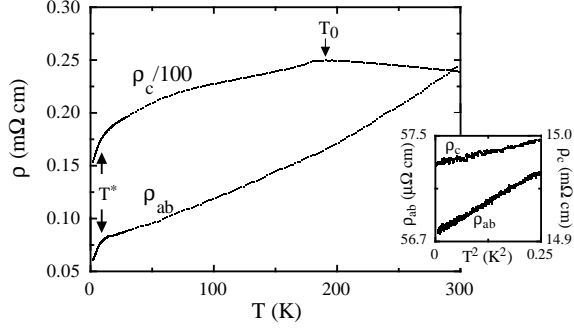


FIG. 2: Temperature dependence of the *ab*-plane electrical resistivity of $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ in both *ab*-plane (ρ_{ab}) and *c*-direction (ρ_c) between 0.05 K and 300 K. The inset is the plot of $\rho_{ab,c}$ versus T^2 .

I). Nevertheless, it is obvious that a sharp decrease occurs in both ρ_{ab} and ρ_c below ~ 10 K, coincident with the characteristic temperature T^* in C_p/T (see the inset of Fig. 1). In light of previous results, we note that such behavior can only be seen if $0.2 < x < 0.5$. [2] In this regime, the low-temperature resistivity has been analyzed using $\rho = \rho_0 + AT^\alpha$, with $\alpha < 2$, leading to the conclusion of non-FL ground state. [5] In contrast, we find that, for $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$, both ρ_{ab} and ρ_c are well described by $\rho = \rho_0 + AT^2$ below ~ 0.5 K as shown in the inset of Fig. 2, characteristic of a Fermi-liquid ground state. The fits from 50 to 500 mK give $A_{ab} = 1.88 \mu\Omega \text{ cm}/\text{K}^2$ and $A_c = 88.8 \mu\Omega \text{ cm}/\text{K}^2$. Similar to what was found in Sr_2RuO_4 , $A_c \gg A_{ab}$, indicating that the quasiparticles essentially form a 2D Fermi liquid. We estimate that $A_{ab}/\gamma^2 = 2.7 \times 10^{-5} \mu\Omega \text{ cm}/(\text{mJ}/\text{mol-K})^2$, comparable to the expected universal value.

Given the heavy-mass Fermi-liquid behavior of $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$, it is natural to expect a large spin susceptibility. Measurements of the magnetic susceptibility χ were performed using a SQUID magnetometer. Fig. 3a displays the temperature dependence of χ at 0.1 T between 2 K and 300 K. Measurements performed in both zero-field-cooling and field-cooling conditions yield identical results. It may be seen that $\chi_{ab,c}$ shows strong temperature dependence. This local moment behavior is strongly in contrast with the relatively *T*-independent Pauli paramagnetism and superconductivity observed in undoped Sr_2RuO_4 . Below ~ 50 K, anisotropy becomes apparent. While $\chi_{ab}(H \parallel ab)$ tends to saturate below ~ 3.5 K, $\chi_c(H \parallel c)$ clearly reveals a peak at $T^* \sim 10$ K. Again, these features resemble those observed in UTb_3 . [11]

Interestingly, both χ_{ab} and χ_c vary smoothly with temperature without noticeable anomaly across T_0 . It was reported that, except for near $x = 2$, χ of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ can be described by a Curie-Weiss (CW) law in a wide temperature regime. [2] For $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$, we plot the susceptibility data as $\chi_{ab,c}^{-1}$ vs. *T* as shown in Fig. 3b. Note that both χ_{ab}^{-1} and χ_c^{-1} vary approximately linearly

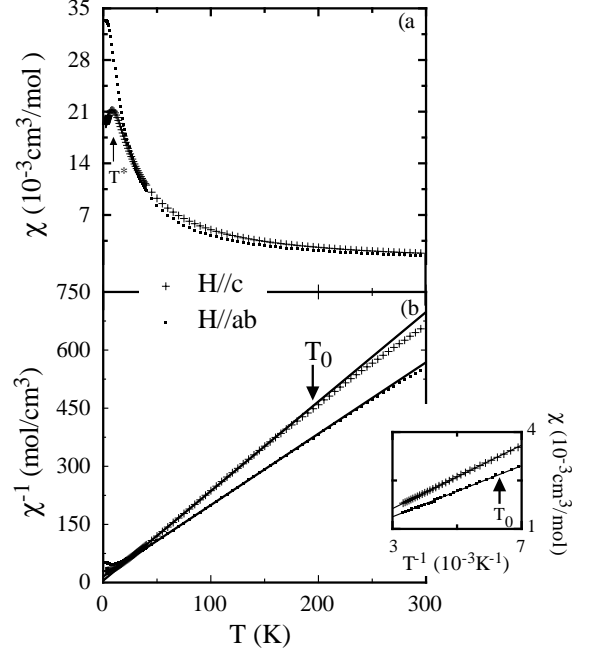


FIG. 3: (a) Temperature dependence of the magnetic susceptibility $\chi_{ab}(H \parallel ab)$ and $\chi_c(H \parallel c)$ at $H = 0.1$ Tesla. Note χ_c reveals a peak at T^* ; (b) Magnetic susceptibility data plotted as χ^{-1} vs. *T*. The solid lines are the fits of experimental data to Eq. (2).

with *T* between 25 K and T_0 . This indicates that $\chi_{ab,c}$ can be expressed as

$$\chi = C/(T - \theta), \quad 25\text{K} < T < T_0, \quad (2)$$

where θ is the CW temperature and *C* is the Curie constant. For $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$, it is well justified to assume that $C = N_A \mu_B^2 g^2 S(S+1)/3k_B$, as the orbital angular momentum for transition metal ions is quenched. [14] Here, N_A is the Avogadro's number, $g = 2$, k_B is the Boltzmann's constant and μ_B is the Bohr magneton. Our fits for the range $25\text{ K} < T < T_0$ (solid lines in Fig. 3b) yield $S = 0.55$ and $\theta_{ab} = -2.4$ K from $\chi_{ab}(T)$, and $S = 0.66$ and $\theta_c = -9.5$ K from $\chi_c(T)$. However, both χ_{ab} and χ_c appear to slowly deviate from the CW behavior above T_0 , and tend to follow a simple Curie law ($\chi \propto T^{-1}$) as demonstrated in the inset of Fig. 3b. This implies that the interactions between local moments become important due to the structural change. The negative θ_{ab} and θ_c suggest antiferromagnetic (AF) spin interactions within the *ab*-plane and along the *c*-direction below T_0 . While evidence for long-range magnetic order has not been found, [6] the peak in χ_c indicates that short-range AF correlation develops along *c*-direction below T^* , consistent with the downturn of the resistivity (see Fig. 2) and the upturn of C_p/T (see Fig. 1).

The above analysis indicates that the magnetic susceptibility of $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ is dominated by the spin susceptibility. Thus, the Wilson ratio, $R_W =$

$\pi^2 k_B^2 \chi_{spin} / 3 \mu_B^2 \gamma$, may be estimated using $\chi_{spin} = \chi$. Given the saturated value $\chi_{ab} = 0.0333 \text{ cm}^3/\text{mol}$ below 3.5 K, we obtain $R_W = 1.7$, exceeding the value of unity expected for free electrons. For comparison, we estimate $R_W = 1.7 - 3.2$ for UPt_3 using the data given by Ref. [11]. It may be seen that the values of R_W are similar in the two systems.

Considering Hund's coupling in the t_{2g} bands and the large crystal field splitting in a $4d$ system, the $S = 1$ configuration is naturally expected for $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$. However, our susceptibility data yield $S = 0.55 - 0.66$, in agreement with previous work.[2] A theoretical investigation[3] suggests that this unusual behavior is driven by the crystal structural distortion (tilting and rotation of RuO_6 octahedra), which narrows the (xz, yz) -subbands and changes the crystal field splitting. In the regime of $0.2 < x < 0.5$, it was proposed that 3 electrons in the (xz, yz) -subbands are localized and produce a net local moment of $S = 1/2$. The remaining electron is in the itinerant xy -band and is responsible for the metallic character. Within this picture, the conduction band is essentially half-filled.

To test the above proposal, Hall measurements were performed by applying current I along the ab -plane ($I \parallel ab$) and magnetic field H along the c -direction ($H \parallel c$). Fig. 4 presents the temperature dependence of the Hall coefficient R_H (hollow circles) at 8 Tesla between 2 and 300 K. Note that R_H is positive and shows strong temperature dependence over the entire temperature range. Similar to χ_c , upon cooling, R_H initially increases and then decreases, revealing a peak around 14 K. For comparison, we replot χ_c into Fig. 4 (solid circles). Remarkably, the two sets of data scale very well between 14 and 300 K without any adjustable parameters. A similar scaling relationship has been seen in UPt_3 . [7] In the latter material, the temperature-dependent R_H above T^* is interpreted as the sum of an ordinary Hall coefficient R_0 , arising from the Lorentz force, and an extraordinary term representing the incoherent skew scattering from local moments, i.e., R_H can be described by

$$R_H = R_0 + 4\pi\chi R_s, \quad (3)$$

where R_s is a T -independent constant. Using Eq. 3 and $\chi = \chi_c$, we fit our R_H data between 15 and 300 K, yielding $R_0 = 7.22 \times 10^{-11} \text{ m}^3/\text{C}$ and $R_s = 2.65 \times 10^{-3} \text{ mol}/\text{C}$. The rather small R_0 suggests the conduction band is close to half-filling, consistent with the theoretical prediction cited above.

Finally, it should be mentioned that R_H of

$\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ resembles that of UPt_3 not only at high temperatures but also in the coherent state. As shown in the inset of Fig. 4, R_H exhibits a T^2 dependence below T^* , as has also been observed in UPt_3 . [7] This implies that the anomalous Hall effect in both systems results from the same scattering mechanism.

In summary, our $C_p(T)$, $\rho(T)$, $\chi(T)$, $R_H(T)$ and X-ray diffraction measurements on $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ indicate a continuous structural transition at $T_0 \sim 190 \text{ K}$, be-

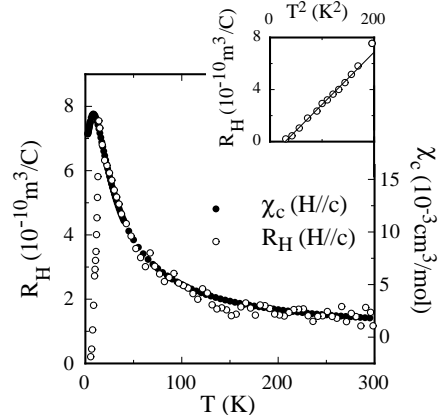


FIG. 4: Temperature dependence of the Hall coefficient R_H (hollow circles) at $H = 8$ Tesla. For comparison, $\chi_c(T)$ (solid circles) is also plotted. Inset illustrates the T^2 dependence of R_H below 14 K.

low which AF interactions between local moments develop. Remarkably, physical properties such as the upturn in C_p/T , the downturn in $\rho(T)$, $\chi(T)$ and $R_H(T)$, and the T^2 -dependence of ρ and R_H below $T^* \sim 10 \text{ K}$ resemble those of the $5f$ HF compound UPt_3 , making $\text{Ca}_{1.7}\text{Sr}_{0.3}\text{RuO}_4$ the only known $4d$ -HF material. This strongly suggests a similar underlying mechanism for the heavy-electron behavior in these two systems, characterized by the large γ , χ and A values.

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